

THE K X-RAY ABSORPTION EDGE OF IRON.

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy
in the University of Michigan.

BY

H. R. VOORHEES.



The K X-Ray Absorption Edge of Iron.

By H. R. VOORHEES *.

[Plate XVI.]

Introduction.

RECENT work in X-ray absorption spectra has shown that on the short wave-length side of the edge there often exists a complicated appearance which has been called the fine structure, or multiple structure of the edge. Early investigators were Stenström †, Fricke ‡, and Hertz §. Lindh ||, in an extended study of the K absorption edges of sulphur, chlorine, and phosphorus, found one or two secondary edges. Coster and Van der Tuuk ¶ reported a secondary edge very close to the K edge of argon. Van Dyke and one of the writers ** found a more complicated structure for the K edge of calcium than had previously been observed for any element. Nuttall ††, working in this laboratory, has recently shown a structure for the potassium and chlorine K edges which is also very complicated.

The valence of the element affects the position of the absorption edge. In the work of Lindh there appeared a progressive shifting of the edge towards shorter wave-lengths as the valence of the element became higher.

The present work was undertaken for the purpose of extending the knowledge of the structure of the K absorp-

* Communicated by J. M. Nuttall, M.Sc.

† Stenström, Diss. Lund, 1919.

‡ Fricke, Phys. Rev. xvi. p. 202 (1920).

§ Hertz, *Zeits. für Phys.* iii. p. 19 (1920).

|| Lindh, Diss. Lund, 1923.

¶ Coster and Van der Tuuk, *Zeits. für Phys.* xxxvii. p. 367 (1926).

** Lindsay and Van Dyke, Phys. Rev. xxviii. p. 613 (1926).

†† Nuttall, Phys. Rev. xxxi. p. 742 (1928).

tion region and also with the hope of showing the effect of valence on this structure. With this in view, iron was chosen because of its convenient wave-length, because of the fact that crystals containing iron are plentiful, and also because iron has two valencies.

Experimental Procedure.

Two methods were used to obtain the absorption : first, crystals containing iron were used both as diffracting crystal and as absorbing medium ; second, screens were made and placed in the path of the beam in the usual manner. The first method has the advantage of forming a very uniform absorber, and of permitting more radiation to reach the plate. It is a very desirable method for long wave-lengths and when good crystals are obtainable. On the other hand, if the crystals are poor and if suitable absorbing screens can be made, the second method gives better results. While crystals containing iron are plentiful, they have not especially good surfaces, and hence in this work the better results were obtained by the second method.

Many of the crystals used were not common in X-ray work, and it was therefore necessary to obtain the crystal-grating constants. This was done by precision measurements on the $\text{CuK}\alpha$ line, as outlined by Siegbahn*. The natural faces of the crystals were used, but in some cases these were polished in an effort to eliminate some of the surface irregularities. This polishing no doubt sacrifices to some extent the sharpness of the fine structure. The absorbing screens were made by mixing the finely-pulverized compound with collodion and spreading the mixture out in thin films to dry. In this manner screens of suitable thickness could readily be obtained. One of the crystals used in the first method was lepidomelane, a mica which contains iron, and which can be split into sheets as thin as 0.01 mm. These sheets served as excellent absorption screens for the second method. The screens for metallic iron were made by rolling a piece of pure electrolytic iron which was obtained from the General Electric Co., through Professor W. P. Davey. The rolling was done between pieces of copper, and fairly uniform screens as thin as 0.01 mm. were made.

A sylvite (KCl) crystal was used in the absorbing screen method. This crystal gave very good reflexion. Its dispersion is somewhat greater than that of calcite.

* Siegbahn, 'Spectroscopy of X-Rays,' pp. 62-64.

A Siegbahn vacuum spectrograph was used for photographing the edges. The reference line used on all the plates was the $\text{FeK}\beta$ line. The WL_2 line was also near, and served as a check. The distance from absorption edge to reference line was measured on a comparator having a least count of 0.005 mm.

In measuring the edge the cross hair of the comparator microscope was brought up just to the point where the blackening begins to decrease. The practice has commonly been to add to this reading one-half the width of the slit. It was found, however, that this correction gave abnormally low wave-lengths in cases where the dispersion of the crystal was small. If no corrections were made, the values for the edge by the two methods were found to agree much better. It was also found that the edge was much less sharp for metallic iron than for the compounds, even though other conditions were the same. This shows that factors other than slit-width may determine the sharpness of the edge. From these considerations it was thought best to omit the correction for the width of the slit. The width of the slit in the crystal method was 0.126 mm. In the screen method, where stronger reflexion could be obtained, it was narrowed to 0.043 mm. This aided in the resolution of some of the details of the structure.

The curves shown in this work are microphotograms taken on a Moll microphotometer. The lens system was modified so as to utilize more of the height of the plate, thus eliminating most of the fluctuations due to the coarse grain of the X-ray plates.

Experimental Details.

The predominant features of the multiple structure are as follows: first, a very sharp principal absorption edge; second, an intense white-line absorption immediately to shorter wave-lengths; third, several secondary regions of absorption, which also sometimes appear as white lines of less intensity. The more striking appearance of the first white line is, however, partly due to the fact that there is less contrast at the secondary edges. The microphotograms show that in many cases the secondary absorptions are really as intense as the principal white line. The blackening between the secondary absorptions by no means approaches in intensity that on the long wave-length side of the principal edge. In the tables this principal edge, which is the one always measured, is designated simply as the K edge. It forms the long wave-length boundary of the principal white line. The short

wave-length boundary is far less distinct. The secondary edges, that is the long wave-length sides of the secondary white lines or bands, are denoted by K_1 , K_2 , K_3 , etc. Certain faint and narrow absorptions that are often found near the secondary edges are designated as K_1' , K_2' , etc. K_1' is between K and K_1 , K_2' is between K_1 and K_2 , and so on. The structure is quite similar for all the compounds of iron.

The structure for metallic iron differs from that for the compounds in that the principal edge is less sharp, as is revealed by the microphotogram of fig. 3 (Pl. XVI.), and there is no white line absorption of note until the K_2 edge is reached. The multiple structure covers a much greater range than in the case of the compounds.

Results of the Crystal Method.

The following crystals were used as diffracting crystals and at the same time as absorbers :—

(1) Iron pyrites, FeS_2 ; (2) Arsenopyrite, AsFeS ; (3) Hematite, Fe_2O_3 ; (4) Epidote, $\text{HCO}_2(\text{Al}, \text{Fe})_2\text{Si}_3\text{O}_{13}$; (5) Lepidomelane, $(\text{K}, \text{H})_2(\text{Mg}, \text{Fe})_2(\text{Al}, \text{Fe})_2(\text{SiO}_4)_3$; (6) Magnetite, Fe_3O_4 .

A summary of the results of the crystal method is given in Table I. The values shown for any one crystal are the average from several plates. The fainter edges are given in parentheses. Fig. 1 (Pl. XVI.), shows a representative plate of this method taken with iron pyrite. In the reproduction of the plate fainter detail is perhaps not evident, but it may be seen in the accompanying microphotogram of the same plate.

The summary of the data shows that the bivalent iron, as it occurs in iron pyrites and arsenopyrite, gives the same wave-length value for the principal edge. The white line for these two compounds measured 7 x.u. in width. Close study of the clearer plates shows, however, that this white line is separated in the middle by a very narrow black line. This indicates the presence of a K_1' edge in this mid-position. Such an edge was found later for the bivalent iron in the absorption-screen method. This faint K_1' edge is probably less distinct in the crystal method because of the wider slit used in that method. The remaining structure of these two crystals is quite the same for both, except that the pyrite crystal, which gave the better reflexion, shows the K_2' and K_3 edges faintly, while in the other they cannot be detected. The hematite and epidote crystals contain trivalent iron. The wave-length of the principal

TABLE I.—Summary of Data for Crystal Method.

 λ = wave-length in x.u. ΔV = energy difference in volts.

Crystal.	λ $\Delta v/R$ ΔV	Edges, K.	White-line width.	K_1'	K_1	K_2'	K_2	K_3'	K_3	K_4'
Pyrite, FeS ₂ (Val. = 2).	λ $\Delta v/R$ ΔV	1738.7	7.1 (4.4)* 2.15 (1.33) 29.2 (18.0)	(1733.2) (1.67) (22.6)	1724.4 4.34 58.9	(1718.2) (6.25) (84.7)	1710.9 8.52 (15)		1698.5 (12.4) (168)	1687.5 15.9 215.0
Arseno-pyrite, AsFeS ₂ (Val. = 2).	λ $\Delta v/R$ ΔV	1738.7	6.7 (4.0)* 2.03 (1.21) 27.5 (16.4)	(1732.8) (1.79) (24.2)	1723.9 4.50 61.0		1712.4 8.05 109.0	1707.9 9.45 128.0		1687.1 16.0 217.0
Hematite, Fe ₂ O ₃ (Val. = 3).	λ $\Delta v/R$ ΔV	1737.2	4.3 1.30 17.6		1725.8 3.47 46.9		1711.5 7.88 107.0	(1707.0) (11.2) (151)		(1686.6) (15.7) (213)
Epidote (Val. = 3).	λ $\Delta v/R$ ΔV	1737.2	4.6 1.39 18.8		1726.1 3.38 45.7		1713.3 7.32 99.0		1696.2 12.7 172	
Lepidomelane (Val. = 2 & 3).	λ $\Delta v/R$ ΔV	1737.5	4.6 1.39 18.8		1723.5 4.26 57.8		1714.1 7.16 97.0	1709.4 8.62 117.0	1695.9 129 174	1689.7 14.8 201.0
Magnetite (Val. = 2 & 3).	λ	1737.6								

Faint signs in parentheses.

* Probable separation point in the white line; barely discernible.

edge for these crystals was 1.5 x.u. shorter than for the bivalent forms. The white line was here found to be 4.4 x.u. in width.

The lepidomelane and magnetite crystals contain both bivalent and trivalent iron. The reflexion from the magnetite crystal was so poor that only the principal edge could be measured. The lepidomelane gave very strong reflexion, but its grating constant was large, and the dispersion was only 55 x.u. per mm. The detail was as sharp as in the crystals having iron of only a single valence.

Results of the Absorption-screen Method.

The absorption-screen method was more fruitful of results because of the excellent reflexion of the (K Cl) crystal used. The slit was now narrowed in order to aid resolution. The dispersion for this sylvite was slightly greater than for calcite.

Absorbing screens were made of the following compounds:—ferrous carbonate, FeCO_3 ; ferric oxide, Fe_2O_3 ; ferrous ferric oxide, Fe_3O_4 ; ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; ferrous ammonium sulphate, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$; and a mechanical mixture of the last two. Thin sheets of lepidomelane were also used as screens, and the metallic iron screen, made as described above, gave the absorption for the uncombined element.

The mineral siderite (FeCO_3) and ferrous ammonium sulphate were chosen because they are rather stable compounds.

Table II. shows a summary of the data obtained by the absorption-screen method, while figs. 2 and 3 (Pl. XVI.) show plates of Fe_3O_4 and metallic iron respectively with their microphotograms. In the case of the mechanical mixture it may be seen that the principal edge is like that for bivalent iron. We should expect this, for if the structures due to both forms are present, the edge due to the trivalent iron would fall in the intense white line due to the bivalent iron, and hence would not appear. Where the bivalent and trivalent iron are both in a single compound, as in the lepidomelane and magnetite, no evidence of a superposition of the two spectra could be found. The wave-length of the principle edge was intermediate between that for the two forms of iron. The white line was very narrow and a distinct K_1' edge was observed. These features indicate that the iron is held in these compounds in such a way as to show neither bivalent nor trivalent spectral characteristics. It rather appears that the iron ions are all alike.

TABLE II.—Summary of Absorption-screen Method. KCl. Crystal.

 λ = wave-length in KCl. ΔV = energy difference in volts.

Screen.	Edges, K.	White- line width.	K_1	K_1'	K_2	K_2'	K_3	K_3'	K_4	K_4'	K_5	K_6
Ferric oxide, Fe_2O_3 .	1736.8	3.9 1.18 16.0	1725.6 3.41 46.1	1731.7 1.85 25.0	...	1713.3 7.20 97.5	1704.5 9.9 135.0	...	...	1686.5 15.6 212.0	...	...
Ferric chloride, $FeCl_3 \cdot 6H_2O$.	1736.8	3.5 1.06 14.4	1725.5 3.44 46.6	1731.1 1.73 23.4	...	1714.9 6.71 90.8	1707.1 9.1 124.0	...	(1682.0) (17.4) (232)	1692.0 13.9 18.8	(1665.7) (22.4) (304)	...
Ferrous carbonate, $FeCO_3$.	1737.9	9.7 .82 11.1	1728.4 2.89 39.1	(1734.2) (1.12) (16.2)	...	(1716.0) (6.69) (90.7)	1709.5 8.7 118.0	...	...	1689.5 15.0 203.0	...	...
Ferrous ammonium sulphate, $FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$.	1737.4	2.7 .82 11.1	1728.0 2.86 38.7	1733.2 1.27 17.1	...	1716.8 6.30 85.3	1706.2 9.6 130.0	...	(1682.1) (17.3) (234)	1695.9 12.8 174.0	(1662.4) (23.7) (321)	...
Mixture of $FeCl_3 \cdot 6H_2O$ & $FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$.	1737.5	3.6 1.39 14.8	1726.8 3.25 44.0		...	1716.5 6.42 87.0	1707.2 9.3 126.0	...	(1683.2) (16.9) (229)	1695.2 13.1 177.0	(1665.7) (22.6) (306)	...
Lepidomelane.	1737.3	2.9 .88 11.9	1727.6 2.95 39.9	1732.1 1.58 21.4	...	1713.8 7.19 97.4	1699.3 11.7 159.0	1709.8 8.44 114	(1683.1) (16.9) (229)	1689.8 14.7 200.0	...	...
Ferrous-ferric oxide, Fe_3O_4 .	1737.4	3.3 1.00 13.5	1726.3 3.38 45.6	(1731.9) (1.67) (22.5)	...	1715.2 6.79 92	1704.7 10.1 136.0	...	...	1688.1 15.3 208.0	...	...
Fe, metallic.	1739.3		1731.4 2.39 32.4	1731.4 2.39 32.4	1721.1 5.64 75.0	1715.2 7.36 100.0	1701.3 11.7 158.0	1706.9 9.9 135.0	1683.4 17.4 236.0	1690.9 14.9 202.0	1663.0 24.0 326.0	(1614.0) (40.7) (551)

Values in parentheses are for faint edges.

Probably the most interesting portion of this work is the spectrum obtained with the screen of pure metallic iron. According to earlier views, which attributed the structure of the edge to the effect of the outer orbits, one should expect to find only a very limited structure for the absorption edge of a neutral element. On the contrary, our plates showed as many as a dozen secondary edges for metallic iron, the structure being distinct to more than 300 volts from the principal edge, with less distinct indications for several hundred volts further. This is a much greater range than has been observed before for the structure of any absorption edge.

It is of note that there is no white-line absorption at the principal edge for metallic iron. As may be observed from the photometer record of fig. 3 (Pl. XVI.), the slope of the edge is more gradual than for the compounds, and the K_1' and K_1 edges appear faintly on this slope. The first appearance of the usual white-line absorption is at the K_2 edge. The wave-length of the principal edge was found to be greater than for either of the ionized forms. Our value of 1739.3 x.u. for this edge is about 0.7 x.u. less than that given by Lindb.

Theoretical Considerations.

Kossel's theory of the fine structure was that the ejected electron may stop in the outer unoccupied orbits of the atom, and thus give rise to secondary edges, depending on the particular orbit in which the transition ends. The edge of shortest wave-length would thus correspond to complete removal of the electron, while the edge of longest wave-length would correspond to a transition to the innermost possible virtual orbit. This theory would account for a structure in the case of metallic iron of only a few volts in width, and at the most for not over 50 volts in the case of the trivalent Fe ion. The structure for the metallic iron here found is even more extended than for the compounds. We therefore think it very likely that multiple simultaneous ionization of the atom occurs under the action of the X-ray beam. G. Wentzel* predicted such a multiply-ionized condition in his discussion of the origin of certain non-diagram lines. Nuttall† gives this multiple ionization as the probable explanation of his results.

* G. Wentzel, *Ann. der Phys.* lxvi. p. 437 (1920).

† J. M. Nuttall, *loc. cit.*

When we attempt to calculate the position of any one of the secondary edges from the standpoint of multiple ionization, we find it difficult because of our lack of knowledge of the transition process in the outer part of the atom. However, since the portion of the spectrum corresponding to the virtual orbits is confined to a narrow region, it is possible to compute the *general* position of the absorption from a knowledge of the energy-levels of the atom.

If the iron atom has one of its K electrons removed to an outer level, its nucleus and K shell *together* then act, in so far as the outer electrons are concerned, like the corresponding parts of a cobalt atom. If an M electron were now to be ejected, it would require energy about equal to that for ejection of an M electron from a cobalt atom, which is about 10.4 volts for an M_I electron, 6.4 volts for an M_{II} or M_{III} electron, and 10 volts for an M_{IV} or M_V electron. If the K electron were entirely removed from the atom, these values would be somewhat more. Now, if one of these M electrons is ejected simultaneously with a K electron, the total energy absorbed will be approximately equal to the sum of that required to eject the K electron from the iron atom and the second M electron from a cobalt atom. If the M electron stops in some of the outer orbits, this energy value will be somewhat less. Thus, by choosing the proper number of electrons to be ejected and the proper stopping-places, it is possible to calculate values which will agree with almost any observed edge. The only point possible to make here at present is that that these computed values agree roughly with the structure found for iron. Thus the value for the K_1 edge is but slightly under the value computed for the ejection of a K electron together with an M_{II-III} electron; the K_2 edge is somewhat less than the computed value for the ejection of a K electron with an M_I electron. Further comparison is hardly worth while until more elements are investigated and until causes for variation in the fine structure are found.

From the multiple ionization viewpoint one might expect to find an absorption corresponding to the simultaneous ejection of a K and an L electron. Many trials were made with different absorption-screens and varying period of exposure to show such an effect. Several plates were obtained which showed two faint edges in the proper location to correspond to the ejection of an L_{II} or L_{III} electron with the K electron.

Kossel's theory will now be compared with the results obtained. According to tables of electron configuration, it

would appear that the N_{II} level is the first one in which a K electron might stop if the selection rule is obeyed. The absorption of energy sufficient to remove the K electron to this level may be considered as the cause of the principal edge. The energy necessary to remove the electron from this N_{II} level to infinity ought to be in the case of metallic iron about equal to the first ionizing potential for cobalt. The first ionizing potential of cobalt is given by Sur* as slightly over 8.5 volts. This would be the width of the virtual orbit effect, and if the white line is thus explained, it should not be more than this width for metallic iron. No evidence of a white line was found, but 8.5 volts would be equivalent to only about 0.2 mm. on our plates, and so narrow a white line might be practically obliterated by the radiation on either side. Applying the same reasoning to bivalent iron, it is found that the width of the white line should correspond approximately to the third ionizing potential of cobalt, which we are probably safe in assuming is not over 35 volts. This would be equal to a width of 8.5 x.u. If we ignore the division of the white line in the case of pyrite and arsenopyrite by the faint K_1' edge, then the entire width of the white line is about 7 x.u. The intense portion of the white line is much narrower than this.

Similarly, the limits for the virtual orbit effect for trivalent iron would be about equal to the fourth ionizing potential of cobalt, which we assume is not far from 50 volts. This is much greater than the observed width of the white line for trivalent iron. A width of 50 volts would reach about as far as the K_1 edge.

It may be, however, that the white line is only another manifestation of multiple ionization, since the second ejected electron might also stop in one of the innermost unoccupied orbits. We could then think of the principal K edge as corresponding to a complete ejection of a K electron, and of the white line as the additive effect of M electrons, moved to higher levels. This view of the principal edge, however, is not in conformity with the low values of $\Delta\nu/R$ for the interval between the L_I edge and the L_{γ_4} line obtained by Miss Chamberlain and Lindsay†. Andrewes, Davies, and Horton‡ are also of the opinion that the principal absorption edge corresponds to the removal of the electron to the first possible unoccupied orbit.

* Sur, Phil. Mag. iv. p. 36 (1927).

† Chamberlain and Lindsay, Phys. Rev. xxx. p. 369 (1927).

‡ Andrewes, Davies, and Horton, Roy. Soc. Proc. ex. p. 64 (1926).

Summary.

The multiple structure for iron, both as a metal and in compounds, has been demonstrated to extend over a range considerably greater than that of any structure previously reported. The magnitude of this range is best explained by simultaneous ejection of electrons from outer orbits together with the K electron. Kossel's hypothesis appears satisfactory only as a possible explanation of the white-line absorption. As has been found previously, the principal edge shifts to shorter wave-lengths as the valence increases. The effect of valence on the multiple structure is small. When bivalent and trivalent iron are mechanically mixed, the expected superposition of the two patterns can be detected, but when the two valencies were in the same chemical compound, as in lepidomelane, no such overlapping could be found.

University of Michigan,
Ann Arbor, Michigan.
June 1928.

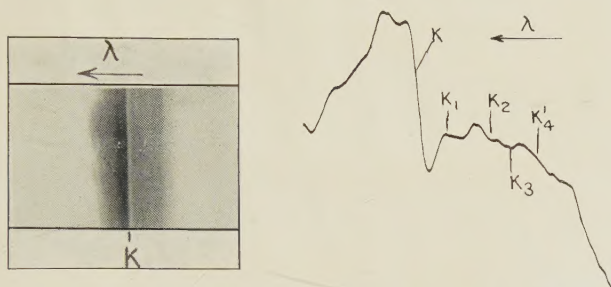
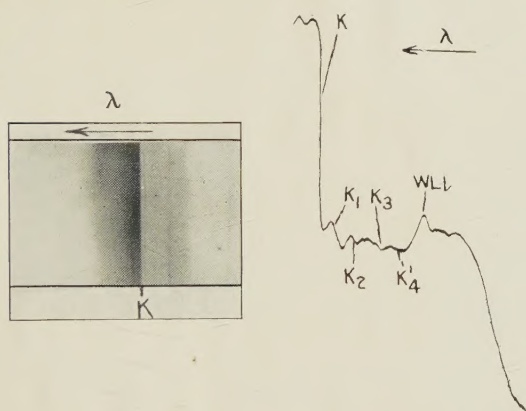
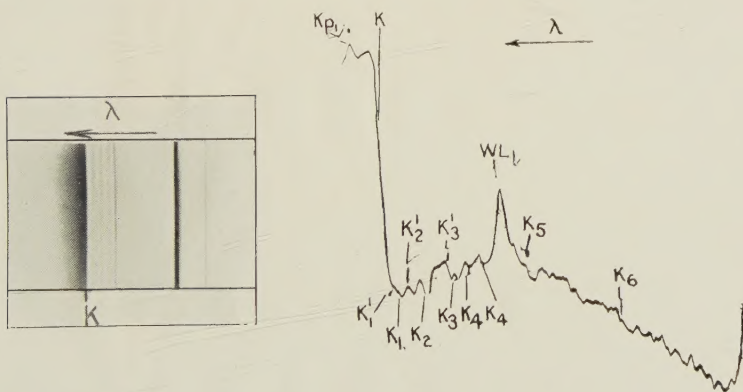
FIG. 1.—K Absorption of Fe in FeS_2 crystal.FIG. 2.—K Absorption of Fe in screen of Fe_3O_4 .

FIG. 3.—K Absorption of Fe in screen of metallic iron.

